The Determination of Molybdenum in Seawater by ICP-AES after Preconcentration by Diethylenetriaminetetraacetic Acid-functionalized Polysiloxane

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A Thesis Submitted in Partial Fulfillment

of the Requirements for the degree of

Master of Philosophy

in

Chemistry

The Chinese University of Hong Kong

June 2002

Acknowledgment

I would like to express my deepest gratitude to my supervisor, Prof. Jimmy C. Yu, who provided me continuous guidance and advice in my research work for the past two years. I would also like to thank Dr Stanton Kok for his unwavering support and encouragement throughout the project. Thanks are also given to Mr. Lee Chi Chung for the collection of NMR, Mr. Chan Chi Ming, Mr. Ng Kwok Kwong, Mr. Wong Wai Hong for their technical supports, and to the colleagues in G52 for their assistance. Finally, I would like to give special thanks to Prof. Raymund W. M. Kwok and Dr Glen K. C. Hui as my examiners. Finally, by no means the least, I gratefully acknowledge the financial support for the present work from the Hong Kong RGC in the past four years.

To all of those not mentioned above, I am deeply indebted, and I express my grateful thanks.

June 2002

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Abstract

This thesis reports a new method for preconcentration and separation of trace amounts of molybdenum in seawater samples prior to the determination by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Diethylenetriaminetetraacetic acid-functionalized polysiloxane was synthesized by the carboxymethylation of amino groups on triamine immobilized polymer, which was prepared by the modification of 3-chloropropylpolysiloxane with diethylenetriamine. The resulting polysiloxane is highly selective and efficient in chelating Mo(VI) at trace ppm levels. It can be used as a column packing material. The polysiloxane column can be reused over ten times without losing its original properties, so it is suitable for preconcentration of molybdenum species in seawater samples before determination. The parameters governing the characteristics of polysiloxane for adsorption of Mo(VI) were investigated. These include the effect of pH, amount of polysiloxane, equilibrium time, adsorption isotherm, maximum adsorption capacity, interfering ions, flow rate, reuse ability and desorption. The precision of the preconcentration method, calculated as the relative standard deviation of seawater samples was 3%. The preconcentration factor and detection limit were 100 and 0.17 ppb, respectively. Measurement results for standard reference materials were in good agreement with the certified values.

二乙烯三胺四乙酸聚硅烷預富集電感耦合等离子體原子發射光譜法測定海水中的鉬

摘要

本論文報導了分離和富集微量鉬的一種新方法，並結合電感耦合等离子體原子發射光譜法(ICP-AES)測定了海水中的微量鉬。3-氯丙基聚硅烷跟二乙烯基三胺反應可得到三胺基固體聚合物，再將該聚合物上的胺基羧甲基化，即可得到二乙烯基-三胺基-四乙酸作為官能團的聚硅烷。這個聚硅烷能夠有效並選擇性地與微量鉬形成螯合物。並且該聚硅烷也可用作柱填料，用該填料製備的富集柱可重複使用十次以上而性能不變。本文所提供的聚硅烷非常適合用于富集海水中的微量鉬。另外，聚硅烷吸附鉬的特性也被研究，其中包括酸鹼度、聚硅烷的量度、平衡時間、吸附等溫線、最大的吸附容量、干擾离子、流速、再生及脫附等。方法的相對標準差為 3%，富集倍數和檢出下限分別是 100 及 0.17ppb。對標準樣品分析所獲得的結果與參考值十分吻合。

CHAPTER 1 INTRODUCTION

1.1 Molybdenum in the Environment

1.1.1 General Chemistry of Molybdenum

Molybdenum is the fourth member of the second transition series and is placed with chromium and tungsten in Group VIA of the Periodic Table. Molybdenum is very similar to tungsten, the third member of the Group, in its chemical properties. However, it is very different from the first member, chromium. Molybdates(VI), unlike chromates(VI), are not strong oxidizing agents. As a transition element, molybdenum shows variable valency and forms many complexes and colored compounds. The outstanding feature of molybdenum is its chemical versatility. It forms compounds in a range of readily interconvertible oxidation states from 2- to 6+, and it complexes with many inorganic and organic ligands, with a particular preference for oxygen, sulfur, fluorine, and chlorine donor atoms[1]. Binuclear and polynuclear species involving bridging ligands (oxide, hydroxide, sulfide) or direct metal-metal bonds between molybdenum atoms, and compounds in which the molybdenum coordination number ranges from four to eight are easily found[2].

1.1.2 Molybdenum in Animals and Plants

In biological systems molybdenum is an essential element for several enzymes important to animal and plant metabolism[3-5]. It is needed for three enzymes in human beings. Sulfite oxidase[6] catalyses the oxidation of sulfite to sulfate, necessary for

metabolism of sulfur amino acids. Sulfite oxidase deficiency or absence leads to neurological symptoms and early death. Xanthine oxidase[7-10] oxidizes hypoxanthine to xanthine and xanthine to uric acid in purine metabolism. Aldehyde oxidase oxidises purines, pyrimidines, pteridines and involves in nicotinic acid metabolism. Low dietary molybdenum leads to low urinary and serum uric acid concentrations and excessive xanthine excretion[8].

As a constituent of the nitrate reductase and nitrogenase of plants, molybdenum is essential in plant growth[11-15]. The reduction of nitrate to nitrite is catalysed by nitrate reductase, a flavoprotein enzyme which contains molybdenum. In the nitrogen fixation[16, 17], nitrogenase catalyses the reduction of nitrogen to ammonia. Legumes need more molybdenum than other crops, such as grass or corn, because the symbiotic bacteria living in the root nodules of legumes require molybdenum for the fixation of atmospheric nitrogen. If molybdenum is insufficient, nodulation will be retarded and the amount of nitrogen fixed by the plant will be limited. If other factors are not limiting, the amount of molybdenum will determine the amount of nitrogen fixed by the plant.

The biochemical importance of molybdenum is due to its chemical properties as mentioned above. It is able to provide facile electron-transfer pathways, a consequence of the easy interconvertibility of different oxidation states. It can form bonds with nitrogen-, oxygen-, and sulfur-donors which are sufficiently strong to permit the existence of stable complexes but also sufficiently labile to permit facile ligand exchange reactions or changes of molybdenum co-ordination number.

1.1.3 Uses of Molybdenum Compounds

Molybdenum-containing catalysts are used for a broad range of reactions[18]. One of the major uses for molybdenum catalysts is in the desulfurization of petroleum, petrochemicals, and coal-derived liquids, in which organosulfur compounds react with hydrogen at the catalyst surface and sulfide ions are removed as hydrogen sulfide. It is also essential for the synthesis of acrylonitrile[19] and oxidation of methanol[20]. Molybdenum disulfide[21] is an important solid lubricant while oil-soluble molybdenum-sulfur[22] compounds have also long been used as antiwear and extreme-pressure additives in lubrication oils and greases. The use of molybdenum compounds in paints, pigments, and corrosion inhibitors has been reviewed[23] and the major use of molybdenum is in the steel industry as alloys. Consequently, it exists in various environmental samples as molybdenum(VI), such as tap water, seawater and river water[24].

Even though molybdenum is much less toxic than many other metals of industrial importance[25-27] and does not constitute a death threat to human beings as a result of environmental pollution, it does have physiological effects on human beings and particularly for animals. High doses of soluble molybdates caused anorexia[28], ataxia[29] and anaemia[30] on animals. High concentration of ammonium dimolybdate was also found to be toxic to fish[31-33].

Therefore, the determination of molybdenum becomes an interesting topic as it has been the subject of regulation recently[24].

1.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

1.2.1 Principle of ICP-AES

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a multi-elemental determination technique that makes use of an argon plasma to excite the emission spectrum of analyte species[34]. It consists of an ionization source and an optical[35] system.

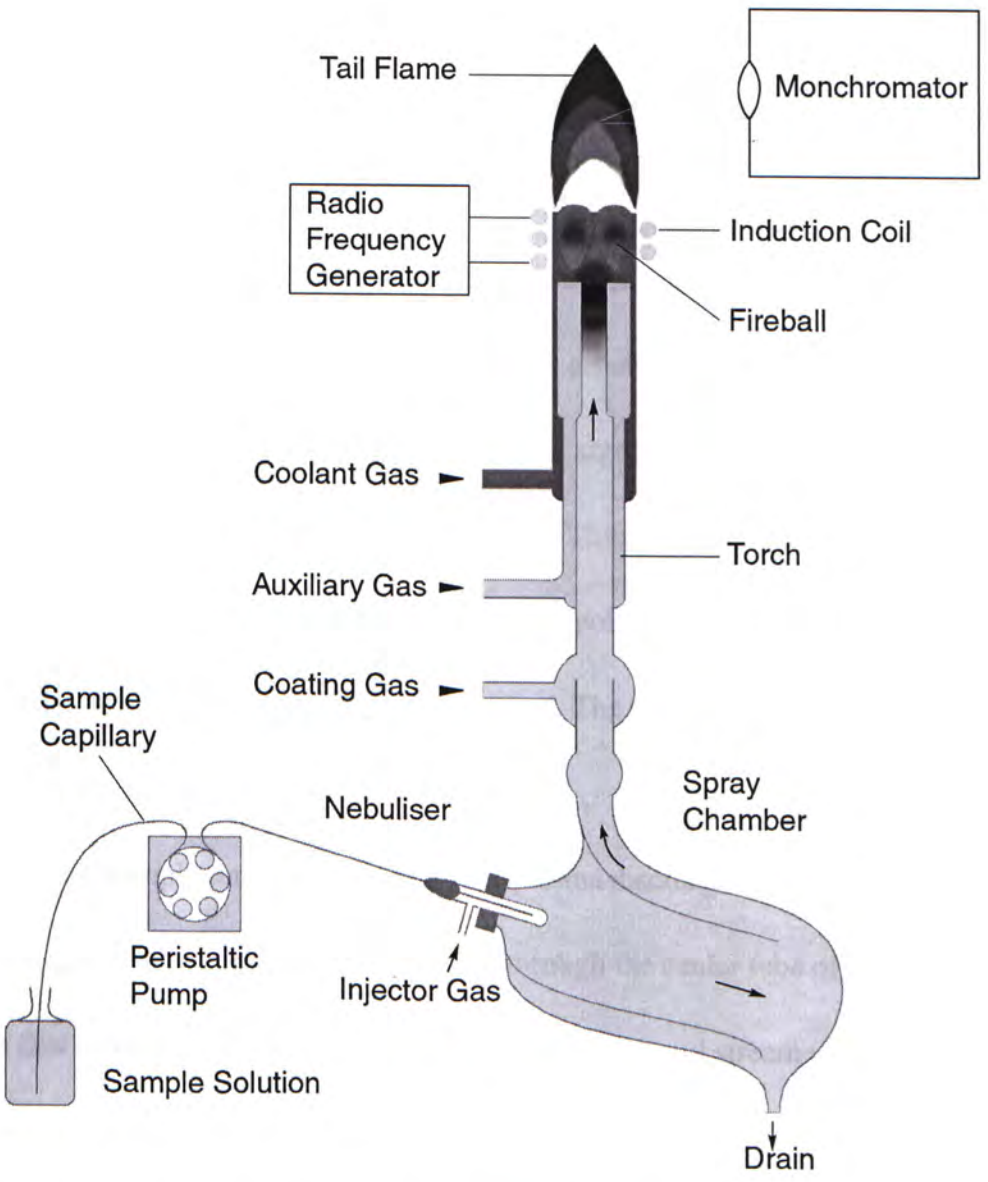


Figure 1. Schematic diagram of a typical ICP-AES

1.2.2 Inductively Coupled Plasma Emission Source

The emission source for the ATOMSCAN 25 spectrometer, which is employed in the experiments, is inductively coupled argon plasma (ICAP). The ICAP source is powered by a 2 kW crystal controlled radio frequency (RF) generator operating at 27.12 MHz. The output from the RF generator is coupled to a water-cooled copper induction coil that is wrapped around the outside of a quartz torch assembly. The largest flow of argon (the coolant flow) passes between the outer and intermediate tubes of the torch. Smaller gas flows pass between the intermediate tube (auxiliary flow), and through the center tube (sample flow).

During plasma ignition, the gas stream is seeded with electrons from an external source, a spark in this case. These electrons are accelerated in a torroidal path by the RF electromagnetic field, and they collide with argon atoms to form more electrons and argon ions, which are in turn accelerated. This process continues until the gas becomes highly ionized (plasma), at which point the discharge is stable and self-sustaining as long as the RF field is applied. The temperature within this torroidal plasma is as high as 10,000 K.

Liquid samples are introduced into the plasma discharge as an aerosol suspended in argon gas. This sample aerosol is carried through the center tube of the three quartz tubes that comprise the torch assembly. The sample aerosol stream passes through the center of the torroidal plasma discharge, where it is desolvated, atomized, and the resultant elements are excited. After excitation, the atoms that comprised the sample emit light at their characteristic wavelengths. This light is transmitted to the optical

system.

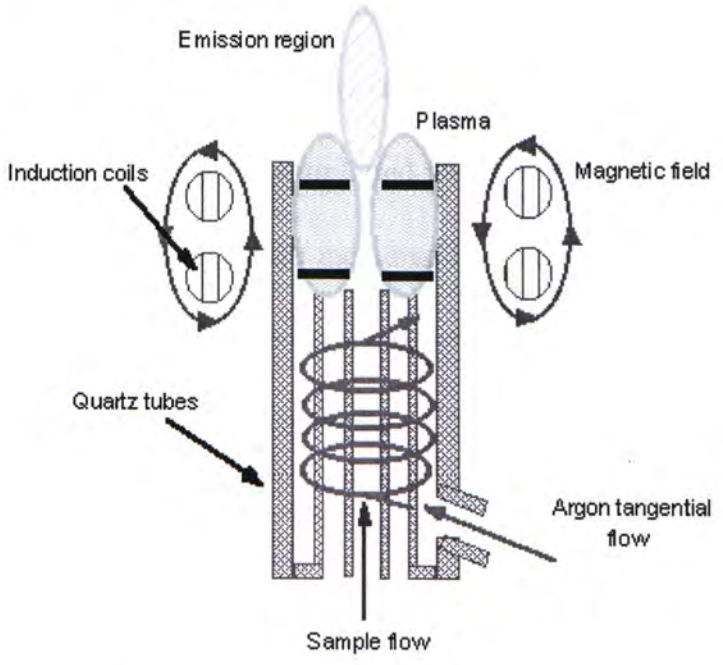


Figure 2. A typical plasma source

1.2.3 Optical System

Light from the plasma emission source is focused onto the entrance slit of the optical system. After passing through the entrance slit, the light is dispersed by a diffraction grating. A narrow range of dispersed wavelengths passes through an exit slit and falls onto a photomultiplier tube (PMT) detector. The detector converts light energy to electrical current, and the magnitude of the current is proportional to light intensity. The current is integrated over a predefined time period, and this integrated change is measured by the detector circuit and passed on to the host computer.

In the monochromator, there are two photomultiplier tubes, of which only one is used at a time. The wavelength of light measured by the detector is controlled by adjusting the angle of the diffraction grating relative to the incident light beam. In a slew scanning monochromator, the grating angle is adjusted by an electromechanical drive mechanism under computer control, and the characteristic wavelengths of the atomic emission from the sample are measured in a rapid sequential fashion. The monochromator slews rapidly between wavelengths and stops to take measurements only at the desired characteristic wavelengths.

1.2.4 Advantages of ICP-AES[34]

Chemical interferences in ICP-AES are fewer than atomic absorption spectroscopy because the residence time of about 2ms at temperatures ranging from 6000 to 8000K in the plasma ensures complete atomization of the sample. The large concentration of electrons from the ionization of the argon also helps to reduce ionization interference effects by maintaining a more or less constant electron concentration in the plasma. In addition, and in contrast to flame sources, the temperature cross section of the plasma is relatively uniform. As a consequence, calibration curves tend to remain linear over several orders of magnitude of concentration.

1.2.5 Disadvantages of ICP-AES

Although ICP-AES is a very sensitive method, its sensitivity is inadequate for the determination of molybdenum in seawater. Spectral interferences caused by the high level of dissolved salts are also a common problem. For example, the presence of OH, PO and SO in high concentrations in the sample matrix can contribute to emission in particular regions both in terms of wavelength and vertical position in the central channel, giving rise to structured background effects[36]. Additionally, physical interferences resulting from the nebulization process also cause difficulties[37]. Therefore, interferences can be minimized by preconcentration methods.

1.3 Preconcentration Method

There are many preconcentration methods for the determination of trace amount of molybdenum in natural samples including the use of chelating resin[38, 39], activated carbon[24, 40], liquid-liquid extraction[41] and solid-phase extraction[42].

For liquid-liquid and solid-phase extraction, both methods are suitable for the UV-visible spectrophotometric determination because the Mo-complexes either dissolve in organic solvents or exist in solid state usually adsorb UV-visible light[41, 42]. For the ICP-AES, the insertion of solid samples directly into the instrument may cause difficulties with calibration, precision and accuracy[43]. High vapor pressure solvents may extinguish the plasma while low vapor pressure solvents may remain in the sample introduction devices.

Since activated carbon is not selective to most metal, complexation between molybdenum and chelating agents such as calmagite reagent[40] or Pyrocatechol Violet[24] are required before the adsorption onto activated carbon. Moreover, the desorption of molybdenum from the activated carbon either by conc. nitric acid or ammonia is time-consuming and alkali may cause precipitation of other metal ions. The chelating resin method is therefore considered to be simpler and less time-consuming than the others.

Preconcentration of Mo(VI) in seawater have been achieved using Muromac A-1[38] and morin chelating resin[39] by other chemists and the concentration of Mo(VI) was determined by AAS and ICP-AES respectively. Limitations of these methods include either complicated setup or desorption by NaOH. Here, we report a simple and

an alternative method for preconcentration of Mo(VI) in sea water using chelating diethylenetriaminetetraacetic acid – functionalized polysiloxane.

1.4 Polysiloxane

1.4.1 Introduction of Silica-gel

Silica gel is an amorphous, highly porous, partially hydrated form of silica which is a substance made from the two most abundant elements in the earth's crust, silicon and oxygen. Today, pure silica gel is manufactured by Patrick's process[44] which consists essentially of releasing silicic acid from a strong solution of sodium silicate by hydrochloric acid. The sodium silicate is usually manufactured by heating sand at a high temperature in contact with caustic soda or sodium carbonate.

$$\text{Sand} + NaOH/\ Na_2CO_3 \rightarrow Na_2SiO_3 + H_2O + 2HCl \rightarrow\ Si(OH)_4 + 2NaCl$$

The free acid quickly starts to condense with itself with the elimination of water to form dimers, trimers and eventually polymer silicic acid. The polymer continues to grow, initially forming polymer aggregates and then polymer spheres, a few Angstrom in diameter. These polymeric spheres are usually referred to as primary silica particles. They continue to grow until, at a particular size, the surface silanol groups (hydroxyl groups attached to the surface silicon atoms) on adjacent primary polymer particles, condense with the elimination of water. This condensation causes the primary particles to adhere to one another and at this stage the solution begins to gel. During this process, the primary particles of silica gel that are formed will have a range of diameters from a few Angstrom to many thousands of Angstrom depending on the conditions of formation such as reaction temperature and pH[45].

Silica gel is an inorganic polymer having siloxane groups (Si-O-Si) in the bulk and silanol groups (Si-OH) on its surface[46]. The latter are responsible for chemical

modifications that may occur on the silica surface. Grafting using organic molecules are the main procedure in order to functionalize silica surface. Normally, this efficient modification process uses alkoxysilanes of the general formula as R-Si-R', where R is methoxy or ethoxy groups and R' is normally a n-propylic carbon chain attached to an organic function[47]. Details of grafting will be described later.

The incorporation of chelating groups onto the silica gel is increasingly finding applications in several areas such as the adsorption of metal cations from organic solvents and water[48, 49], the use as a stationary phase in high-performance liquid chromatography[50] and the application as catalysis for chemicals reactions[51]. The immobilization has been directed mainly at silica gel, because its surface has been investigated from both physical and chemical aspects and it offers many advantages over organic surfaces. Firstly, a large variety of silylating agents can be used[52-54], allowing a myriad of pendant functional groups to be immobilized on the support. Secondly, functional groups immobilized on silica gel react more easily than those on an organic support because this matrix has a large number of crosslinking bonds which may require hours to reach equilibrium[55]. Finally, silica, as well as other inorganic supports, are unreactive to organic solvents and have a high thermal resistance[56].

In the majority of the immobilization procedures involving pure silica gel, this carrier is previously heated at 423 K for several hours under vacuum, in order to eliminate physisorbed weakly-bound multilayers of water molecules[57, 58]. However, an alternative route to immobilize some alkoxysilxanes molecules can be obtained by means of the sol-gel process. In this case, $Si(OEt)_4$ is normally used as a

skeletal-forming agent for silica gel[59, 60]. By selecting a suitable silylant agent or by using a sequence of reactions, one can anchor molecules with a high capacity to adsorb metal cations on the surface.

1.4.2 Introduction of Sol-gel Processes

Sol-gel processes are methods of forming dispersed inorganic materials in solvents, through the growth of metal-oxo polymers[61, 62]. The chemistry is based on inorganic polymerization reactions. Metal alkoxides [$M(OR)_z$, where M = Si, Sn, Ti, Zr, Al, Mo, V, W, Ce, etc.; OR, an alkoxy group OC_nH_{2n+1}] are used as molecular precursors which lead to metal-oxo polymers through hydrolysis and condensation reactions.

The first step in sol-gel synthesis is the hydroxylation of the metal alkoxide, which occurs upon hydrolysis of the alkoxy groups as follows[63]:

$$M\text{-}OR + H_2O \rightarrow M\text{-}OH + ROH$$

Reactive hydroxy groups are firstly generated and then undergo polycondensation reactions via two competing mechanisms:

(a) Oxolation: the formation of an oxygen bridge:

$$M\text{-}OH + M\text{-}OX \rightarrow M\text{-}O\text{-}M + XOH$$

(X = H or alkyl group)

(b) Olation : the formation of a hydroxo bridge:

$$M\text{-}OH + HO\text{-}M \rightarrow M(OH)_2M$$ (X = H or alkyl group)

Metal–oxo based oligomers and polymers capped by residual hydroxo and alkoxy groups are the result of these two equilibrated reactions.

The structure and morphology of the resulting metal-oxo macromolecular networks are dependent on the respective rates of different reactions. Rearrangement reactions then occur, leading preferentially to weakly branched polymers. When these structures reach a macroscopic size, a gel in which solvent and free polymer are entrapped is obtained. The gel state is not the only possibility. Other final forms, such as colloidal solutions or precipitates, can be obtained. The formation of gels or colloidal species reflects different growing processes and different polymer–solvent interactions. Control of the nature of the intermediate species through the reaction conditions is essential to tailor-made the final structures. The reactivity of the metal alkoxide[64] (nature of M and R), the hydrolysis ratio (H_2O : M), the solvent, the reaction temperautre, the use of complexing agents or catalysts are the main parameters used to achieve control over the size and morphology of the resulting materials. Starting from molecular precursors, more and more condensed species are obtained, leading to colloidal 'sols' and then to 'gels'.

1.4.3 Hybrid Inorganic-organic Sol-gel Materials

Hybrid inorganic-organic sol-gel materials are made by mixing organic and inorganic components. It can be prepared by two approaches[65]. Organic molecules can just be embedded into an inorganic material, or vice versa. Alternatively, the organic and inorganic groupings can be linked by stable chemical bonds. The latter approach

requires precursors in which the organic group is bonded to the oxide-forming element, i.e. Si, in a hydrolytically stable way.

In principle, any element forming compounds suitable for sol-gel processing can be used for the formation of the inorganic structures. Silicon is currently the most often used element. The choice of the organic group R is nearly unlimited. The only condition is that the group is hydrolytically stable or reacts with water in a controlled way. More than one organic group R can be bonded to the same metal, although such precursors are rarely used in sol-gel chemistry. A more challenging possibility is the use of precursors in which the organic group R bears some functionality. The relevant precursors are of the type $(R'O)_nE\text{-}X\text{-}A$ where E represents the metal centre, A represents the functional organic group, and X is a chemically inert spacer linking A and the metal alkoxide moiety. Precursors with a direct chemical bond between A and $E(OR')_m$ normally cannot be employed owing to its low stabiliby[65]. In our project, the chloro hybrid materials was prepared by $Si(OEt)_4$, the most commonly used type of precursors in the sol-gel processes and $Si(OMe)_3(CH_2)_3Cl$. It was then subjected to modification by other chemical reagents.

Silica aerogels made of only $Si(OR')_4$ are very hydrophilic, due to residual Si-OR' and Si-OH groups. However, the use of $RSi(OMe_3)$/ $Si(OMe_4)$ mixtures (R = alkyl or aryl) resulted in hydrophobic silica hybrid, being insensitive toward moisture. This hydrophobizing effect of the organic groups is caused by the suppression and replacement of the Si-OMe and Si-OH groups[66-68]. During the preparation of purely inorganic materials, organic groups in sol-gel materials can control the reaction rates

of the reactants, the rheology of the sols, or the homogeneity and micro-structure of the derived gels.

1.4.4 Advantages Using Sol-gel Preparation of Organomodified Silica

There is a range of possible methodologies exists for attaching organic functionality to the surface of a silica support. They include grafting of functional organosilanes, surface chlorination and subsequent displacement, direct sol-gel preparation of organomodified silicas and post functionalisation of existing organic groups at the surface[69].

Grafting

This remains the most popular method, mostly due to its simplicity, at least in terms of experimental procedures. The silica is reacted with an appropriate organosilane in a suitable solvent, typically toluene at reflux, although ethanol at room temperature is also effective in some cases. The resulting solid is collected and washed.

This method is versatile and relatively rapid, with many silanes being commercially available. However, loadings of organic groups on the surface are usually less than 1 $mmolg^{-1}$. Moreover, drawbacks include the formation of several surface species resulting from binding via one, two or three Si-O-Si groups as shown in Figure 3, attachment of oligomeric silanes, and the presence of physisorbed material[70].

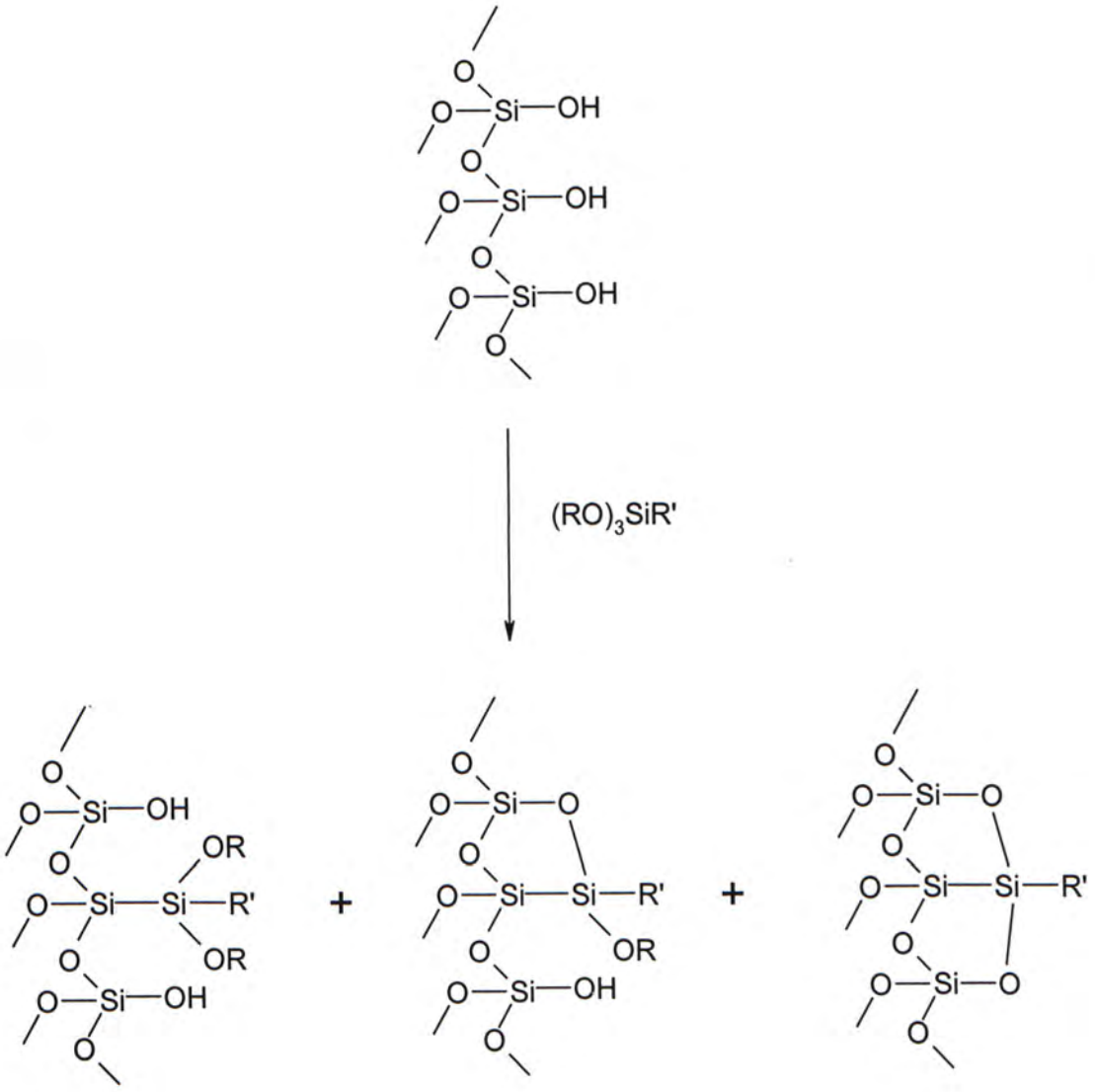


Figure 3. Simplified grafting reaction at a silica surface

Surface chlorination and subsequent displacement

This is a much less frequently used method, although it has advantages of forming a direct Si-C bond at the surface and precludes the formation of surface bound oligomers and variable modes of attachment. Groups are robustly bound, and are

typically less prone to leaching than those attached via grafting[69]. However, the technique is more complicated, requiring the reaction of silica with the chlorinating agent and converting surface hydroxyls to Si-Cl bonds. It is typically achieved using thionyl chloride at reflux[71], or with CCl_4 in a fluidised bed reactor[72] at 400-450 °C. The Si-Cl material thus produced is reacted with a solution of a Grignard reagent or an organo-lithium species, leading to displacement of the Cl and the formation of a Si-C surface bond. The main drawback of this method is that the requirement for strongly nucleophilic reagents limits the functionality which can be successfully attached.

Sol-gel preparation of organomodified silicas and post functionalisation

When compared with other methods, sol-gel preparation of organomodified silicas followed by post modification appears to be more attractive. It gives materials which are rigid and have good thermal and hydrolytic stability[73]. Such materials can, in principle at least, contain a much higher density of ligand groups than can be achieved by surface silylation, and the anchorage of the ligand groups is generally more secure[74] and less prone to leaching than those attached via grafting. The formation of surface bound oligomers and variable modes of attachment are also prevented. Moreover, ligand groups are placed in the most accessible positions[73] which is good for the adsorption of metal ions.

1.5 Chelating Resin

A chelating resin is a polymeric solid substance with a mainframe containing active functional groups, capable of interacting with metal ions to form co-ordination bonds. The sorption of metal ions on chelating resins is mainly due to complex formation within the resin, which distinguishes it from conventional ion exchange. The complexation behaviour of polymer-supported ligand is different from the corresponding low molecular weight analogue, because of distinct characteristic of the polymeric support[75]. Hence, the complexation parameters of functional ligands are determined by the polymeric matrix and are controlled by the nature of the polymeric backbone, the nature and extent of the crosslinking agent, the nature of the ligand and its distribution and accessibility in the polymer. The versatility of these polymers is attributed to the triple function of ion exchange, chelate formation and physical adsorption. Chelating resins containing aminophosphonate[76], dithiocarbamate[77], hexylthioglycolate[78], iminodiacetate[79], isothiouronium[80] as functional groups are generally employed for heavy metal sorption. Examples of chelating groups and their application for selective preconcentration of inorganic elements have been reviewed by Kantipuly et al[81].

The functional group atoms responsible for chelate formation usually include nitrogen, oxygen and sulphur. The inclusion of suitable functional groups into a polymeric matrix promotes interactions with specific metal ions under favourable conditions. The selective removal of elements from aqueous effluents depends both on elemental speciation and the chelating properties of the polymer. For example

Chelex-100[82], which has a polystyrene backbone containing iminodiacetic acid [-CH_2-N($CH_2COOH)_2$] functional groups and is widely used in trace analysis for preconcentration of heavy metals. However, chelex-100 shrinks as its ionic form and pH change. It swells 100% in changing from hydrogen to a monovalent salt form. In addition, the resin has an affinity for alkali and alkaline earth elements that causes matrix problems during atomic emission spectrometric determination of trace metals and decreases the resin's capacity[83]. Although molybdenum(VI) adsorbs on Chelex-100 under the same condition as many common transition metal ions, its desorption is not quantitative as other metal ions[84].

In this project, we report the synthesis of a new chelating resin having diethylenetriaminetetraacetic acid functional groups. The stability, selectivity, reusability and capacity for metal ions have been studied.

1.6 Scope of the Work

The research work of this thesis focused mainly on the development of a new chelating resin for the preconcentration of Mo(VI) in seawater prior to the determination by ICP-AES. It was divided into two parts.

In the first part, the synthesis of the diethylenetriaminetetraacetic acid polysiloxane was described. The characterizations of the polysiloxane were achieved using NMR spectrometer, FT-IR spectrometer and elemental analysis.

The second part studied the application of diethylenetriaminetetraacetic acid polysiloxane in the preconcentration of Mo(VI). The parameters governing the characteristics of polysiloxane for preconcentration of Mo(VI) were investigated. These included the effect of pH, amount of polysiloxane, equilibrium time, adsorption isotherm, maximum adsorption capacity, interfering ions, flow rate, reusability and desorption. The developed method was verified by analyzing certificate standard reference materials and determination of recovery of Mo(VI) spiked into seawater samples.

CHAPTER 2 EXPERIMENTAL

2.1 Apparatus and Instrument

A Thermo Jarrell Ash ATOMSCAN 25 ICP-AES was used. The measurement parameters are shown in Table 1.

Table 1: Operation conditions of ICP-AES

Inductively coupled plasma:	
RF frequency	27.12 MHz
RF power	1150 W
Plasma argon flow	14 L/min
Auxiliary argon gas flow	1.0 L/min
Nebulizer argon pressure	30 psi continuously
Spray chamber	Glass
Torch	Quartz
Nebulizer	Teflon and sapphire
Peristaltic pump rate	100 rpm
Atomic emission spectrometer:	
Monochrometer	0.75 meter crossed Czerny-Turner monochrometer
Photomultiplier tube detectors	R427 solar blind and R889 IR enhanced
Monochromator grating	Composite grating with 2400 and 1200 lines/mm
wavelengths	202.030nm with background correction
Reference for monochromator calibration	Mercury lamp
Data acquisition	
Integration time	10 seconds
Number of repeats	5 times for assay

A four-channel peristaltic pump (Alitea U4-MIDI) was used for the delivery of sample solutions through the packed columns. An Orion's model 290A pH meter was used to measure the pH values.

Nuclear magnetic resonance (NMR) spectra were measured with a Bruker DPX300 NMR spectrometer at 75.47MHz (^{13}C) in NaOD using a 5-mm dual frequency ^{13}C probe. All chemical shifts were recorded in ppm relative to tetramethylsilane. Infrared spectra (IR) were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer with KBr pellets containing about 5mg of the sample. Elemental analyses were carried out by MEDAC Ltd, Department of Chemistry, Brunel University, Uxbridge, UK.

2.2 Chemicals

Tetraethylorthosilicate and 3-chloropropyltrimethoxysilane were obtained from Acros Chemical Company and were utilized without purification. Diethylenetriamine and sodium chloroacetate were purchased from Aldrich Chemical Company. Diethylenetriamine was dried with sodium under reflux, purified by vacuum distillation and stored under nitrogen before use. Ammonium molybdate tetrahydrate was purchased from BDH Chemical Company and was used to prepare the Mo(VI) stock solution. Molybdenum reference standard solution (1000 ppm, in dilute HNO_3) was obtained from AccuTrace^{TM}. All the other metal salts were obtained from BDH and were of analytical grade. High-purity water (18MΩ-cm) was prepared by using a deionized water system (Milli-Q, Millipore Corp.) while Ultratrace nitric acid was purchased from Tedia Company in Canada. Laboratory glassware was kept overnight in a 10% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust free environment.

2.3 Samples

Two certified reference materials (CRMs), NASS-2 Seawater (Open Ocean) and CASS-2 Seawater (Coastal), were obtained from the National Research Council of Canada (NRCC, Ottawa, Canada). Seawater samples were collected in April 2001 at the Tolo Harbour, Hong Kong. They were filtered through 0.45μm Millipore filters immediately after sampling. The filters were acid-cleaned 24 hours prior to use. This removed any particulate matter, which might interfere with the subsequent plasma analysis and cause blockages in the proposed preconcentration system. The samples were preserved on site by the addition of 5 mL of 65% nitric acid per 1 L of seawater to prevent deposition of metal ions onto the surface of the container. It has been reported that at low pH values (pH 1-2), most metal ions are more stable[85]. The samples were then stored in darkness, in pre-cleaned polypropylene bottles and the analysis was complete within two weeks after sampling.

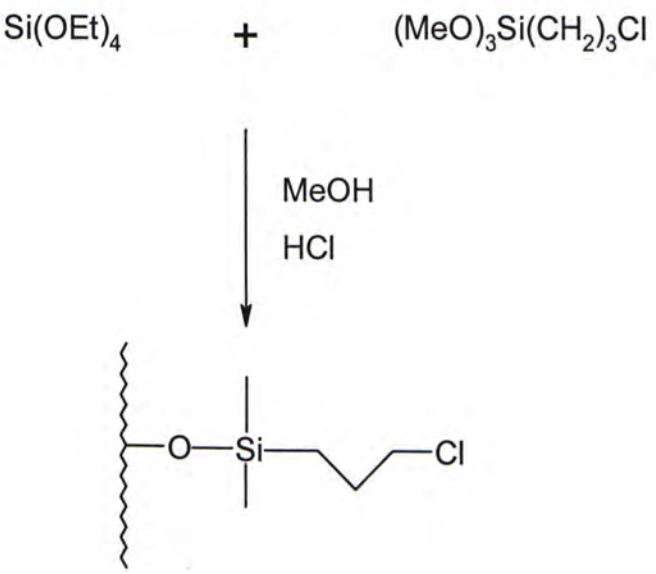
2.4 Procedures

2.4.1. Preparation of Diethylenetriaminetetraacetic Acid-functionalized Polysiloxane

2.4.1.1 Preparation of Silica Precursor[86-88]

The 3-chloropropyl-functionalised polysiloxane was prepared from tetraethylorthosilicate (20g, 96mmol) and 3-chloropropyltrimethoxysilane (19g, 96mmol) in methanol (60mL), hydrochloric acid (0.42M, 6mL) was added as a catalyst. The mixture was allowed to solidify overnight and then crushed, ground, dried at 100°C, followed by washing with methanol, water and ether (Scheme 1).

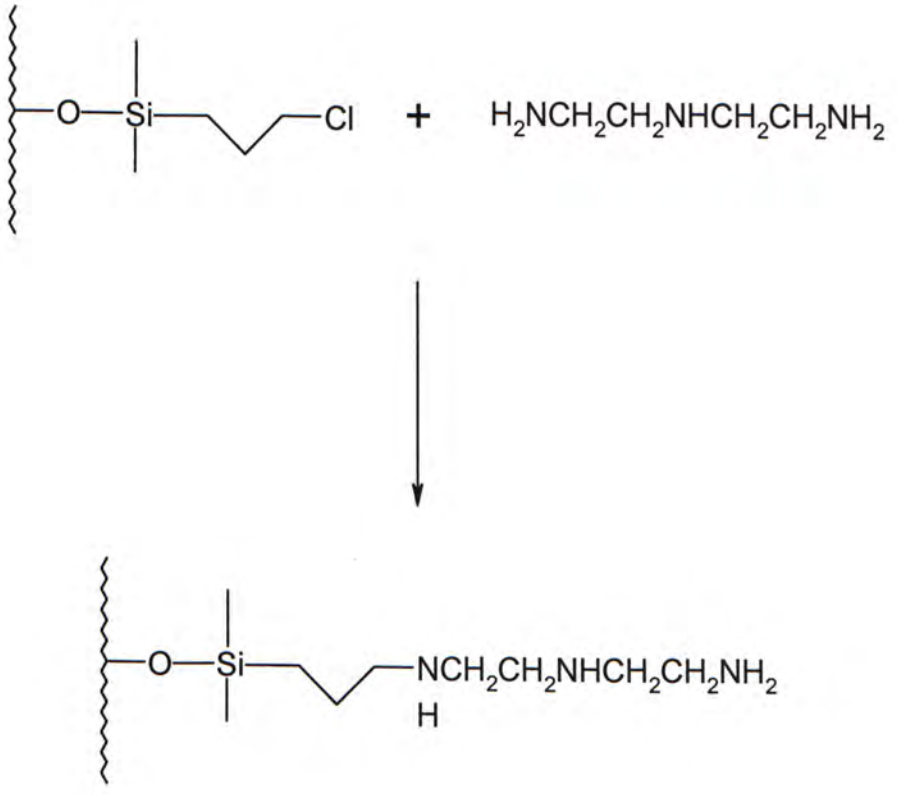
Scheme 1



2.4.1.2 Functionalisation with Diethylenetriamine[88, 89]

The polysiloxane-immobilized diethylenetriamine ligand system was prepared by refluxing an excess of diethylenetriamine (300mL) with the 3-chloropropyl-functionalised polysilxoane (15g) under nitrogen for 24 hours. The mixture was cooled and the solid phase was filtered off. The solid was washed successively with 100mL portions of 0.05M aqueous sodium hydroxide, water, methanol and diethyl ether. Finally, the product was dried at a pressure of 0.01mmHg at 80°C overnight (Scheme 2).

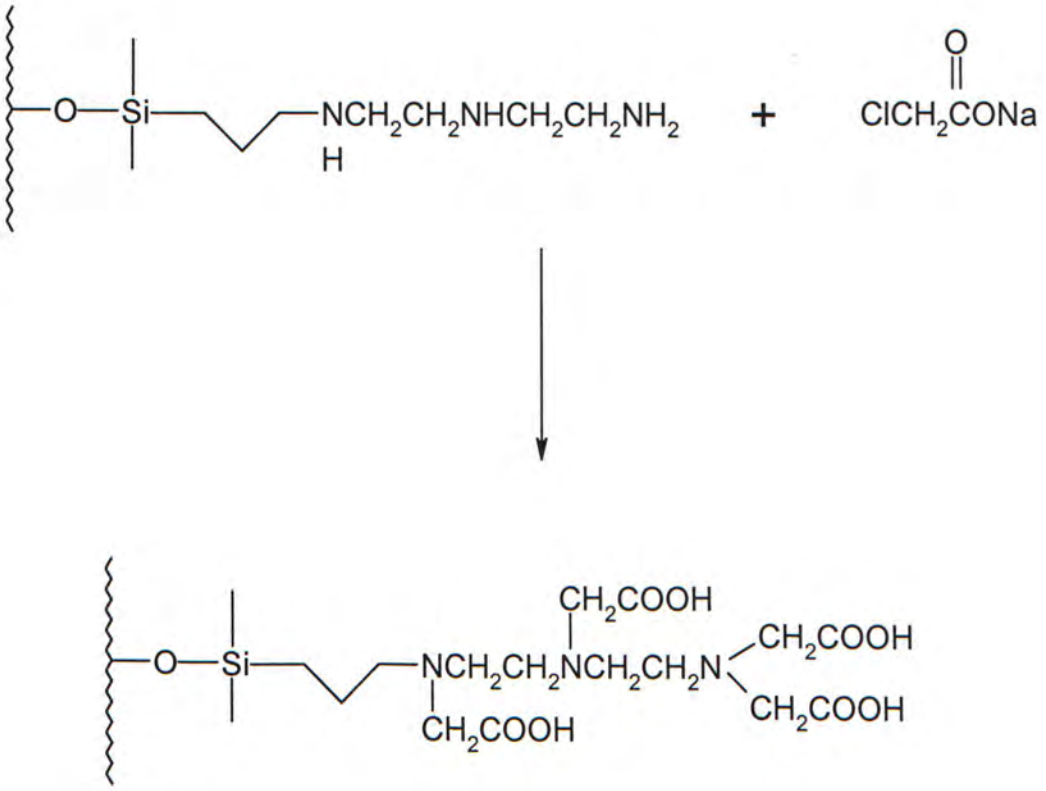
Scheme 2



2.4.1.3 Carboxymethylation of the Amine Groups of the Polysiloxane[90]

The triamine-functionalised polysiloxane (10g) reacted with an excess amount of sodium chloroacetate solution (25g in 100mL water). The mixture was stirred at room temperature for 24 hours. The solid was filtered and washed several times with water and 50mL of ethanol (Scheme 3).

Scheme 3



2.4.2 Preconcentration and Determination of Molybdenum

Both the batch[91] and column methods were used to study the parameters governing the characteristics of polysiloxane for preconcentration of Mo(VI) in the aqueous solution.

Batch experiments

2.4.2.1 Optimum pH for Adsorption[92]

Molybdenum solutions (25mL, 1000ppm) were pipetted to 50mL propylene capped-tubes. The pH of the molybdenum solution was adjusted over the range 1-7 by nitric acid prior to equilibration. The polysiloxane (0.1g) was added to the tubes and the mixture was left for 24 hours at room temperature with occasional shaking. After equilibration, the polysiloxane was filtered and the concentration difference of molybdenum solution was determined by ICP-AES.

2.4.2.2 Amount of Polysiloxane Required for Sorption of Trace Amount of Molybdenum[40]

Molybdenum solutions (1000mL, 50ppb) were adjusted to the optimum pH before mixing with different amount of polysiloxane. The mixture was stirred for 2 hours at room temperature. The minimum amount of polysiloxane for complete adsorption was found and the concentration difference of molybdenum was determined by ICP-AES after filtration.

2.4.2.3 Equilibrium Time[93-95]

The effect of shaking time on the adsorption of molybdenum was determined by equilibrating the polysiloxane (0.05g) with molybdenum solution (500mL, 50ppb) at different time intervals and at the optimum pH. The amount of molybdenum in the solution was determined by ICP-AES after filtration

2.4.2.4 Total Adsorption Capacity[96-97]

The adsorption capacity of the polysiloxane on Mo(VI) was determined by a batch process in an excess amount of metal ion under the optimum pH. The total adsorption capacity was calculated as:

Total adsorption capacity ($mmolg^{-1}$)

$= (C_0 - C_A)\ V/\ W$

where C_0 = initial concentration of molybdenum in mmol, C_A = equilibrium concentration of molybdenum in mmol, V = volume of the solution and W = weight of the dry polysiloxane.

2.4.2.5 Adsorption Isotherm of Molybdenum

The isotherm of adsorption was obtained using the batch method[98-101]. The polysiloxane (0.1g) was equilibrated with molybdenum solution (20mL) in the concentration range 10-2550ppm. The mixture was shaken to equilibrate with occasionally shaking for 24 hours at room temperature. The amount of molybdenum remaining in the filtrate was determined by ICP-AES.

2.4.2.6 Desorption Studies[94, 96]

The lowest concentration of nitric acid for complete desorption of Mo(VI) was determined. The loaded polysiloxane was added to an aqueous solution of nitric acid (1-3M) and the mixture was allowed to equilibrate for 3 minutes. The polysiloxane was filtered and the Mo(VI) ions in the filtrate were determined by ICP-AES.

2.4.2.7 Effect of Foreign Ions on Preconcentration[39,102]

The influence of foreign ions (Na(I), K(I), Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II), Pb(II), Fe(II), Fe(III),Cd(II), Sn(IV), W(VI), Al(III), Sr(II), Ba(II), Cl^-, F^-, Br^-, I^-, ClO_4^-, SCN^-, SiO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$ and HPO_4^{2-}) usually found in sea water were examined. Manifold amounts of the foreign ions as interferents were added separately to the molybdenum solution (250mL, 10ppb), and the recovery of molybdenum from polysiloxane was studied.

Mini-column experiments

2.4.2.8 Preparation of the Mini-column[103]

Figure 4 shows the construction of a simple glass column (0.5id., 2cm height) packed with 80mg of polysiloxane. Packing of the material was achieved under vacuum (0.05mmHg).

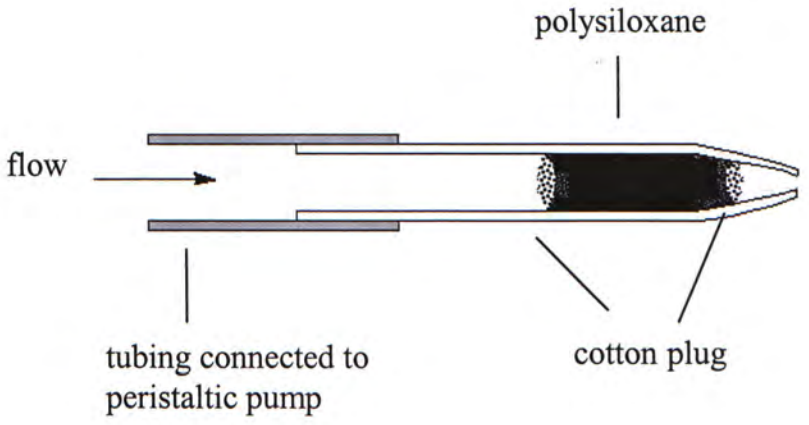


Figure 4. The packed mini-column.

2.4.2.9 Effect of Flow Rate[104]

The effects of flow rate on the adsorption of Mo(VI) on polysiloxane were investigated with the mini-column connected to a peristaltic pump. The standard solutions (50mL, 10ppb) at the optimum pH were passed through the columns at different flow rates, then the recovery of Mo(VI) from the polysiloxane was determined.

2.4.2.10 Reusability of the Mini-column[98, 105]

The stability of the polysiloxane column was evaluated by repetitive adsorption and elution of Mo(VI). 16 cycles were repeated and the recovery of molybdenum from the column was determined each time.

2.4.2.11 Preconcentration Factor and Detection Limit[40, 106, 107]

The preconcentration factor was determined by decreasing the amount of nitric acid used for desorption of molybdenum from polysiloxane while keeping the total amount of loaded metal ions constant (1000mL, 10ppb). For the detection limit, it was defined as three times the standard deviation of five replicate measurements of the blank.

2.4.2.12 Determination of Mo(VI) in Seawater by ICP-AES

The seawater sample containing trace amounts of Mo(VI) was passed through the column at the optimum flow rate. After washing with 10mL of water, the Mo(VI)

adsorbed onto the column was eluted out by nitric acid. The concentration of Mo(VI) in the effluent was determined by ICP-AES.

CHAPTER 3 RESULTS AND DISCUSSION

3.1 Characterization of Diethylenetriaminetetraacetic Acid-functionalized Polysiloxane

There are two methods for the preparation of functionalised, cross-linked polysiloxane[73]. Both involve the hydrolytic condensation of $Si(OEt)_4$ and $RSi(OR')_3$ (R' = Me or Et; R = a functionalised alkyl group), the difference lying in whether the ligand group introduced into the group R before or after the polymerization. For example, 3-chloropropyltrimethoxysilane is commercially available. Other functionalised starting materials could be prepared by replacement of the organochlorine group before co-condensation with tetraethylorthosilicate. However, this preparation is not trivial as the reaction is required to carry out under anhydrous conditions and the product also has to be separated and purified before use. Therefore we prefer to prepare polymers containing 3-chloropropyl groups and to introduce the ligand groups in a second stage. The tetraethylorthosilicate acts as a cross-linking agent, giving porous, solid polymers. In the absence of it, oligomeric siloxanes will be formed instead[108].

The 3-chloropropyl silica precursor could be prepared in the presence of acid or dibutyl-tin diacetate catalyst. Even though aqueous sodium hydroxide can catalyze many sol-gel reactions, it is not suitable for the co-condensation between tetraethylorthosilicate and 3-chloropropyltrimethoxysilane owing to uncontrolled rapid gelation and the low chlorine-content of the products[73]. As the tin compound

may incorporate in the polysiloxane[109] even with the relatively small amounts of catalyst employed, hydrochloric acid is however more practical and clean. A series of experiments established that the most satisfactory mole ratio of HCl to $Si(OEt)_4$ was 0.1 : 1[109]. A further advantage of acid catalyst is that the polymers have great mechanical strength and they are much less prone to degradation of the particles by magnetic stirrers[89].

In the presence of hydrochloric acid catalyst, a stable polymer from 1 : 1 mixtures of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3Cl$ was formed even though self-condensation of $(MeO)_3Si(CH_2)_3Cl$ could not be prevented[74, 86]. A more open and less cross-linked structure of 1 : 1 mixtures also allows more extensive substitution by other functional groups. The results of elemental analysis are shown in Table 2.

Table 2: Elemental composition of polysiloxanes

Code	%C	%H	%N	%Cl	C-ratio[a]
1	15.20	3.51		15.39	
2	26.48	6.20	12.50	0.15	1.05
3	25.06	5.20	7.89	0.63	

[a]C-ratio = molar ratio of total carbon to carbon bound to nitrogen (C_N) and to chlorine (C_{Cl}): $C_{tot}/ (C_N + C_{Cl})$

The data show that the percentages of carbon, hydrogen and chlorine in 3-chloropropyl polymer are almost the same as those reported in literature[86]. Solid state ^{13}C and ^{29}Si NMR spectroscopy, based on cross polarization (CP) and magic-angle spinning (MAS) techniques, have been used by Maciel[87] to identify the structure of 3-chloropropyl polysiloxane. The signals of solid state ^{13}C NMR spectrum are at 10.9, 27.3 and 47.8ppm respectively. ^{13}C NMR is also useful for the characterization of pendant groups provided that the polysiloxane could dissolve in a solvent. In the presence of NaOD, Si-C bonds are not hydrolyzed because of the specific properties of silicon, i.e. low Lewis acidity and a rather unpolar Si-C bond[65]. On the other hand, the hydrolysis of siloxane network (Si-O-Si bond) produces a leaching solution of 3-chloropropyl polysiloxane[110]. Figure 5 shows the spectrum of leached material with three methylene carbon signals at 12.0, 27.7 and 49.2ppm which match quite well with that obtained by Maciel. This confirms the attachment of the pendant groups on the polysiloxane.

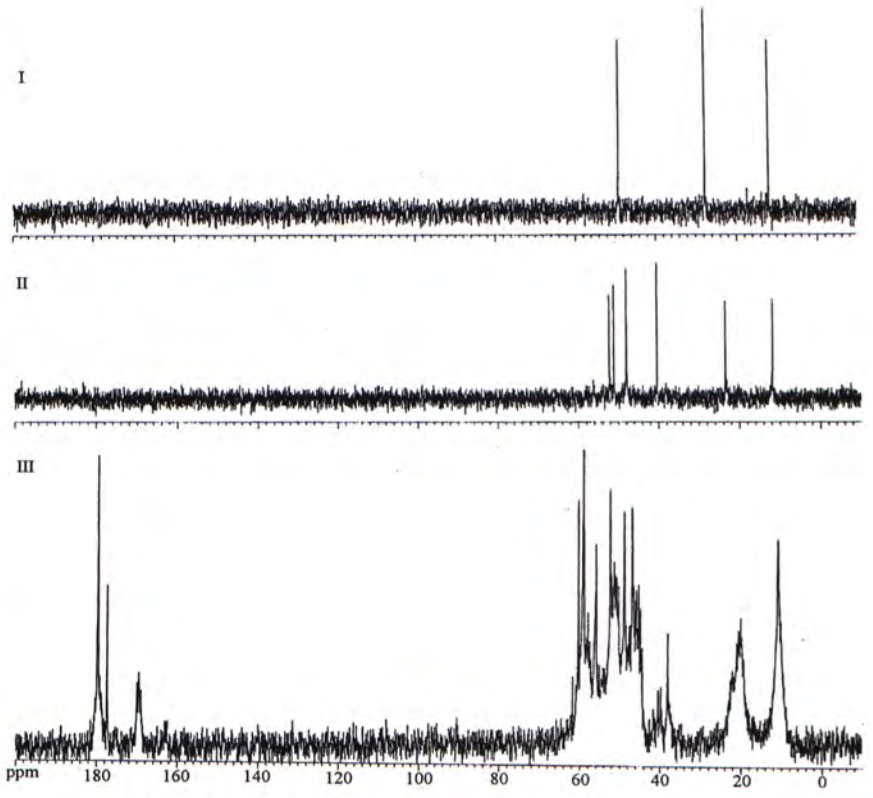


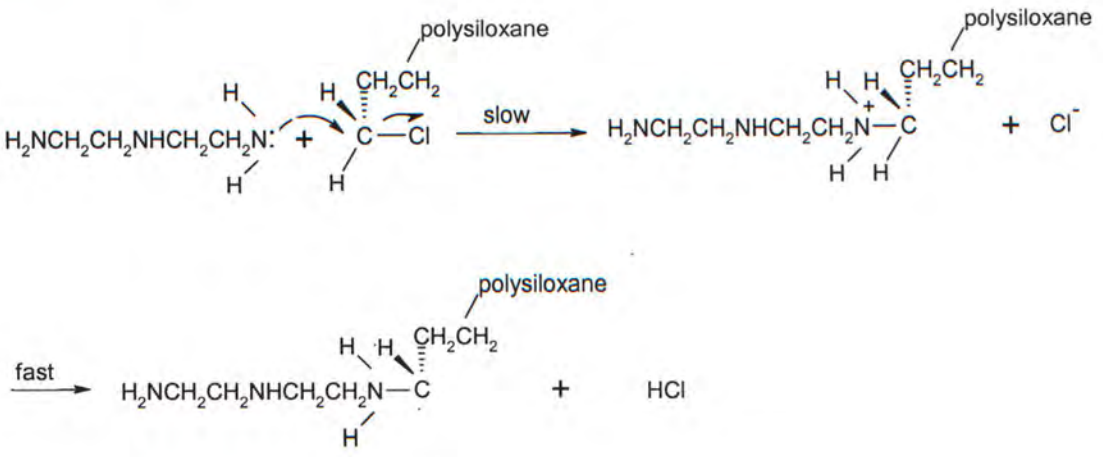
Figure 5. ^{13}C NMR spectra of (I) 3-chloropropylpolysiloxane, (II) polysiloxane immobilized triamine system, (III) diethylenetriaminetetraacetic acid-functionalized polysiloxane.

The pendant organochlorine groups on the polysiloxane were converted into triamine system by reacting with diethylentriamine. Diethylenetriamine was dried before use to prevent hydrolysis on the silica precursor due to traces of moisture. By calculating the molar ratio of total carbon to the sum of that bound to nitrogen (7 atoms) and to chlorine (3 atoms) of polysiloxane-immobilized triamine system, a ratio of 1

was obtained. This indicated that all the chlorine groups reacted only with the diethylenetriamine, and hydrolysis did not occur. Even though traces of chlorine remained unreacted, the amount is negligible.

The reaction between silica precursor and diethylenetriamine follows S_N2 mechanism. For S_N2 reaction, the nucleophile must approach the alkyl chloride from the side opposite the bond to the leaving group. This approach may be hindered by substituents on both the carbon that is being attacked and the nucleophile. The two hydrogen substituents of propyl chloride offer little resistance to approach of the triamine system, so almost all the chlorine groups could be substituted by the amine based on the elemental analysis results. However, it was found that the terminal amine group of the diethylenetriamine approached the silica is relatively easier than the secondary amine[88]. This is because greater steric hindrance of the secondary amine makes it less favourable for the S_N2 reaction, as shown in Figure 6.

Substitution by primary amine



Substitution by secondary amine

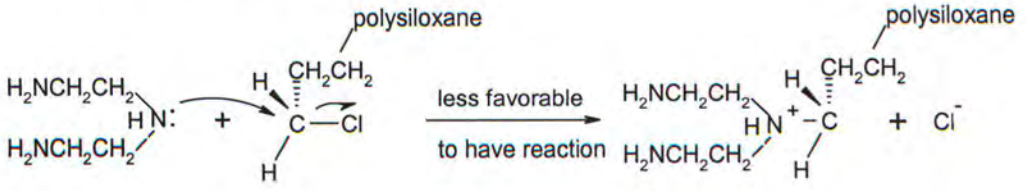


Figure 6. Proposed mechanism of S_N2 substitution by primary amine and secondary amine.

By using the solid state ^{13}C-NMR and ^{15}N-NMR, Maciel confirmed that the main chemical form of the polysiloxane is S-$CH_2CH_2CH_2NHCH_2CH_2$ $NHCH_2CH_2NH_2$ rather than S-$CH_2CH_2CH_2N(CH_2CH_2NH_2)_2$[88]. Since low resolution solid state ^{13}C-NMR was used in that study, the spectrum showed only four signals at 12.0, 24.3 and 43.0ppm with a very intense peaks at 51.9ppm which involved four carbon atoms on the amine ligands. For the solution-state NMR, seven peaks were clearly identified

(11.7, 23.3, 40.3, 47.9, 48.0, 51.2 and 52.2ppm). These peaks correspond well with the seven carbons on the silicon-alkyl chain. Had the other form, $S\text{-}CH_2CH_2CH_2N(CH_2CH_2NH_2)_2$, been produced in the synthesis, one would expect a pattern in which a signal due to carbon atoms attached to the tertiary amine nitrogen should appear at ~58ppm[111].

One more evidence to confirm the main structure of polysiloxane-immobilized triamine system is based on Maciel's ^{15}N-NMR spectrum. Two signals at 18.2 and 33.6ppm have been found which are expected for the primary and secondary amine groups, respectively. The absence of a tertiary amine signal, which would be expected to occur at about 50-55ppm[112-115] confirms the absence of $S\text{-}CH_2CH_2CH_2N(CH_2CH_2NH_2)_2$ on the polysiloxane.

In general, solid-state NMR is very useful in characterizing the polysiloxane network, such as the extent of attachment of organic moieties to the polysiloxane and the degree of crosslinking of the whole network[87, 88]. For example, ^{13}C-NMR could provide information on the degree of hydrolysis of ethoxy and methoxy group of $Si(OEt)_4$ and $(MeO)_3SiCl$ by identifying the corresponding carbon signals. It was found that the hydrolysis of $Si(OEt)_4$ and $(MeO)_3SiCl$ was not complete in the presence of either hydrochloric acid or butyl-tin catalyst. However, diethlenetriamine could act as a good catalyst for hydrolysis of the residual ΞSi-OEt or ΞSi-OMe. This allows the formation of polysiloxane framework with a higher degree of crosslinking. For solid state ^{29}Si-NMR, one can identity the $Si(\text{-}O\text{-})_4$, $RSi(\text{-}O\text{-})_3$, $(\Xi SiO)_2Si(OR')_2$,

$(\equiv SiO)_3SiOR'$ and siloxane bridges $(\equiv SiO)_4Si$, respectively, where R' = Et or H and R is the organic group containing the ligand.

To deduce the interaction between Mo(VI) and the ligand groups on the polysiloxane, solution-state NMR can be used to detect the changes of the functional groups in the reactions. Although solution-state NMR cannot identify the siloxane network directly, it does provide information for characterizing the structure of the alkyl pendant groups on the polysiloxane. Most of our samples are well dissolved in aqueous NaOD solution although sonication may be required for a faster dissolution.

In the carboxymethylation of amino groups on polysiloxane-immobilized triamine system, it can be assumed that an almost complete conversion is obtained[90]. The FT-IR spectrum in Figure 7 shows the carboxyl group vibration as a sharp band at $1632cm^{-1}$. For the solution-state ^{13}C-NMR, three broad peaks are clearly observed between 169.1 and 179.9ppm. These peaks correspond to the carbonyl carbons. Relatively broad peaks are observed because the carboxymethylated polysiloxane does not dissolve completely in NaOD and it may also be inhomogeneous caused by a large variation of local fields around the measured nuclei. The peaks at about 11, 20 and 38ppm correspond to the carbon atoms on the propyl chain.

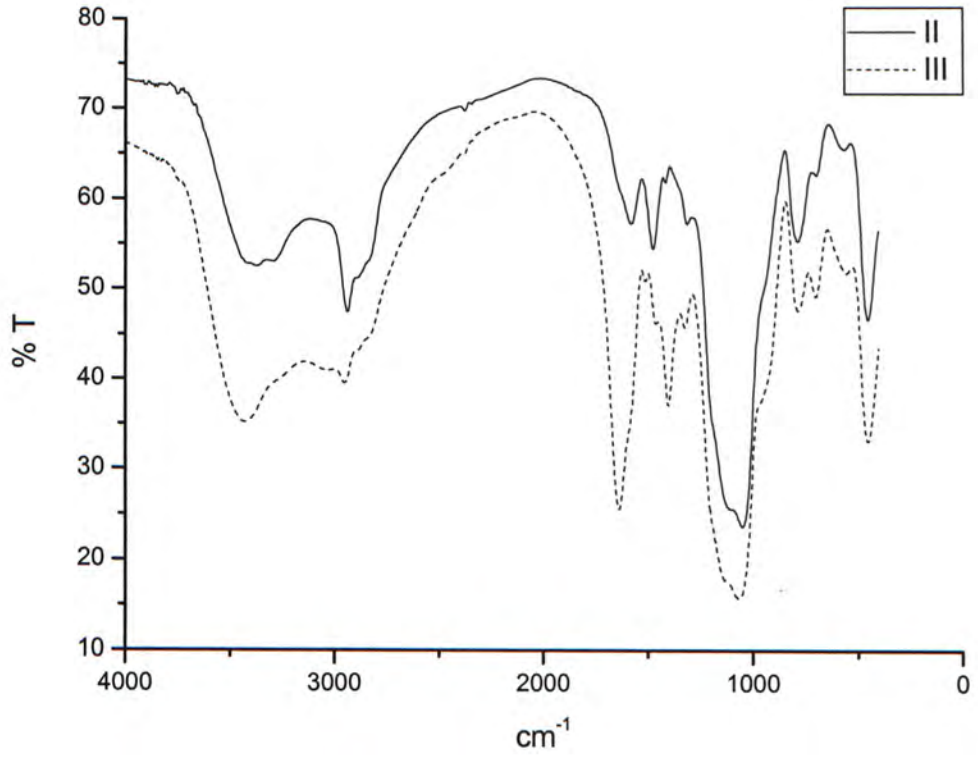


Figure 7. IR spectra of polysiloxane (II) polysiloxane immobilized triamine system, (III) diethylenetriaminetetraacetic acid-functionalized polysiloxane.

3.2 pH Dependence of Mo(VI) Ion Uptake

In order to obtain optimum conditions for preconcentration, the adsorptivity of Mo(VI) on polysiloxane over a pH range of 1 – 7 was examined. The adsorption affinity of Mo(VI) as a function of the pH is shown in Figure 8. The optimum pH was found to be 3.

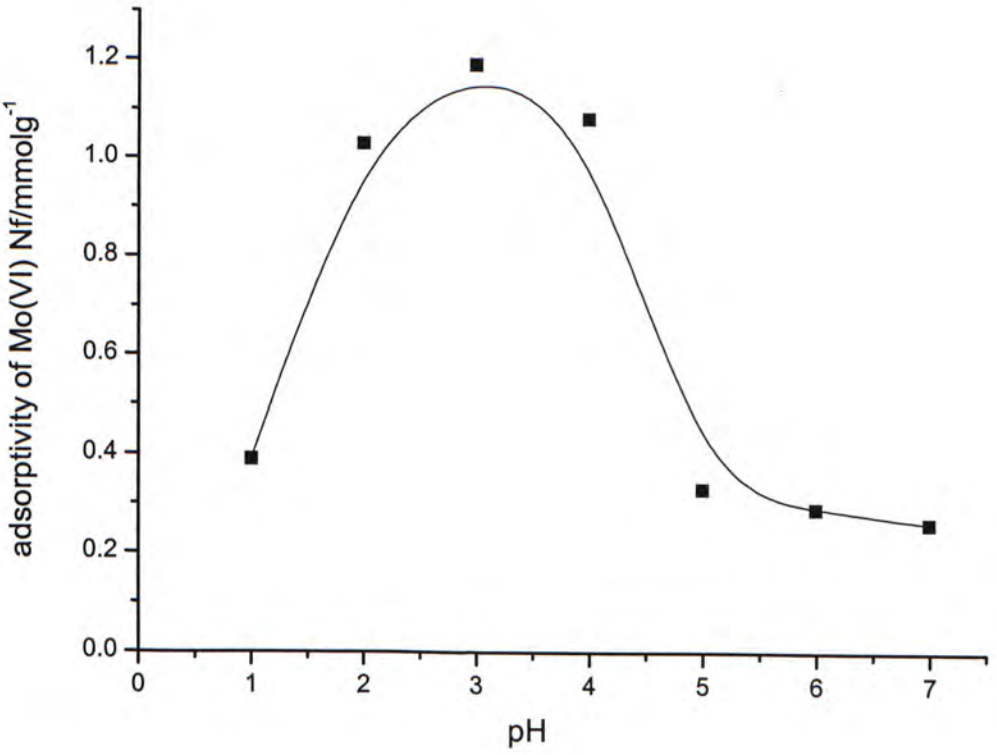


Figure 8. Effect of pH on the adsorption of Mo(VI).

3.3 Amount of Polysiloxane Required for Adsorption of Trace Amount of Mo(VI)

In order to determine the amount of polysiloxane for the complete adsorption of trace amounts of Mo(VI), polymers with mass range from 3 to 20mg were tested. Figure 9 shows that a mass of 15mg is sufficient for complete retention. Therefore, the diethylenetriaminetetraacetic acid functionalized polysiloxane is an economical method for preconcentration. The use of such a small amount of polysiloxane also increases the efficiency in packing the column, and the back-pressure resulting from the packing materials is also reduced.

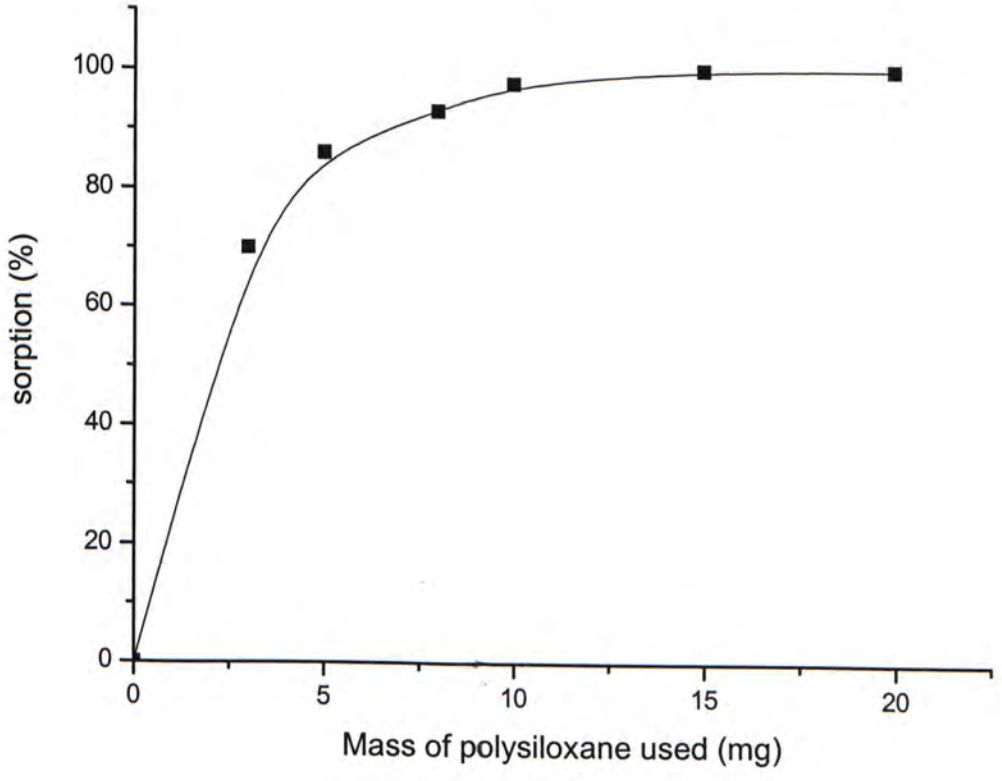


Figure 9. The amount of polysiloxane required for adsorption of Mo(VI).

3.4 Equilibrium Time

The equilibrium time was investigated by batch experiments at pH 3. Figure 10 shows the adsorption of Mo(VI) by polysiloxane as a function of contact time. It is notable that Mo(VI) is $\geq$ 90% extracted in 3 minutes. The fast extraction rate indicates that there is high availability of the chelating groups and most of them are present on or near the surface of polysiloxane which allows equilibrium to be reached rapidly. Therefore, the diethylenetriaminetetraacetic acid functionalized polysiloxane is highly suitable for the preconcentration of trace Mo(VI) from aqueous solutions.

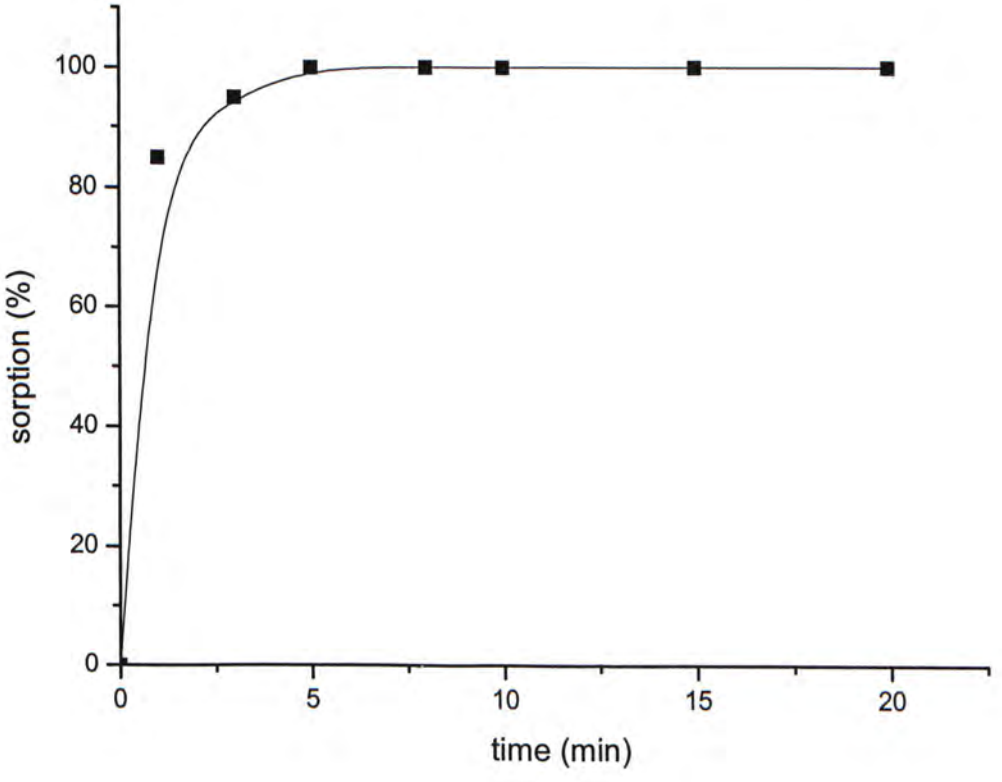


Figure 10. The equilibrium time on the adsorption of Mo(VI).

3.5 Total Adsorption Capacity

The total adsorption capacity of the polysiloxane for Mo(VI) was determined by a batch process under the optimum pH. It was calculated as:

Total adsorption capacity ($mmolg^{-1}$)

$= (C_0 - C_A)\ V/\ W$

where C_0 = initial concentration of molybdenum in mmol, C_A = equilibrium concentration of molybdenum in mmol, V = volume of the solution and W = weight of the dry polysiloxane.

It was found that the loading capacity calculated from the difference between the metal ion concentration before and after desorption was 1.2mmol/g.

3.6 Adsorption Isotherm of Molybdenum

The pendant groups disposed on the structure enable the polysiloxane to interact with the Mo(VI) due to the presence of seven hard basic centres. The ability of this surface to extract Mo(VI) from aqueous solution was evaluated by measuring the adsorption isotherms. Under equilibrium conditions, the exchange processes at the solid-liquid interface can be characterized by the number of moles adsorbed (N_f) per gram of polysiloxane. This value was calculated from the initial number of moles of Mo(VI) added (n_i) and those at the equilibrium point (n_s) for a mass (m) of the polysiloxane, in grams, by applying the expression:

$$N_f = \frac{n_i - n_s}{m}$$

Profiles of the adsorption isotherms for Mo(VI) at pH 3 are shown in figure 11, representing the number of moles adsorbed versus the concentration of the supernatant under equilibrium conditions. When the adsorption profile reaches a plateau, a monolayer is supposed to be establised. The data of the isotherm reveal that the adsorption process conforms to the Langmuir model, as proposed for a series of systems[47, 101, 116].

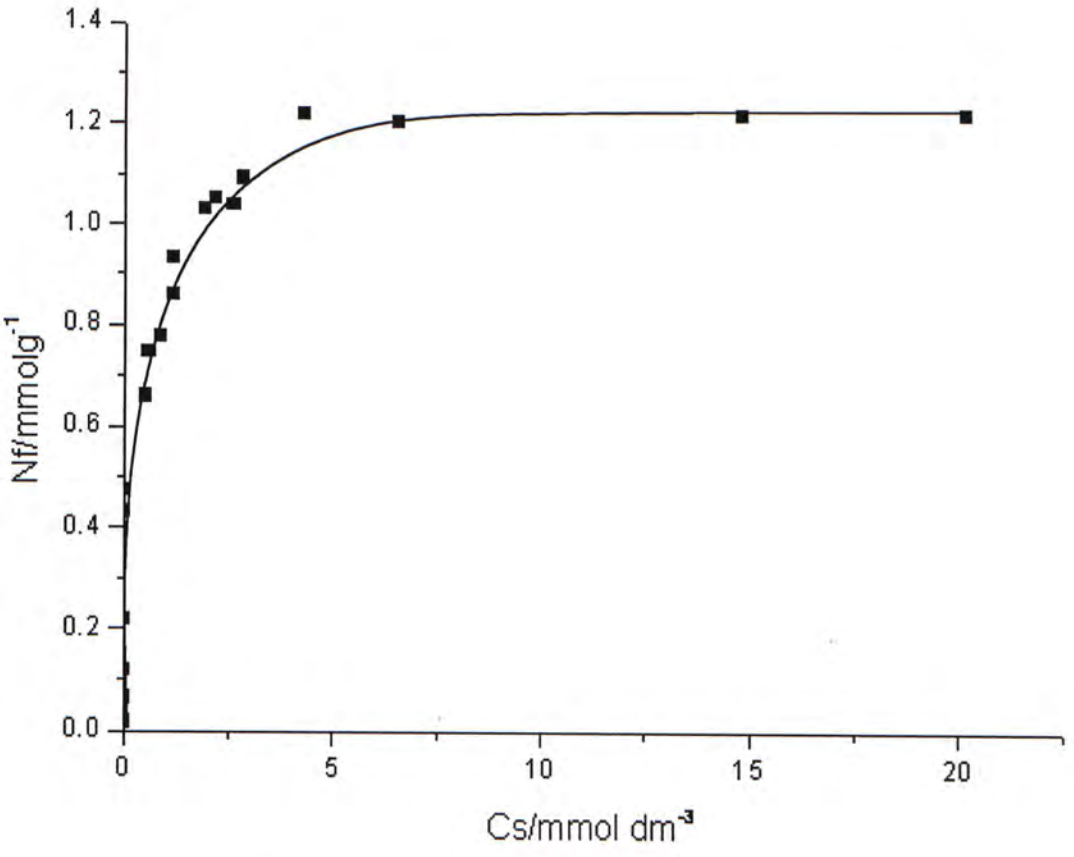


Figure 11. Adsorption isotherm of Mo(VI) on polysiloxane surface.

A modified Langmuir equation can be conformed to this kind of adsorption isotherm as represented below:

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b}$$

From this expression, C_s is the concentration of Mo(VI) at equilibrium ($moldm^{-3}$), N_f as defined before ($molg^{-1}$), N_s is the maximum amount of Mo(VI) adsorbed per gram of surface ($molg^{-1}$), which depends on the number of adsorption sites, b is a constant. Based on the linearized form of the adsorption isotherm derived from plots of C_s / N_f vs. C_s, the constant N_s values was calculated[117]. In Figure 12, the graph shows

an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. The N_s is found to be 1.23mmolg^{-1} which matchs well with the results obtained from the total adsorption capacity. This process gives an indication of the thermodynamic stability of the complexes formed on the surfaces. Even though the N_s value does not demonstrate a clear stoichiometry related to total ligand sites available, as observed for other bidentate basic centres[118, 119], we are still able to propose the interaction between Mo(VI) and the ligand groups on the polysiloxane. Based on the structural features of the pendant groups attached to the inorganic backbone, it is expected that nitrogen and oxygen atoms are responsible for the interaction. The chemistry of Mo in aqueous phase is more complex due to the multiple oxidation states and the different species that can be formed from each one[120].

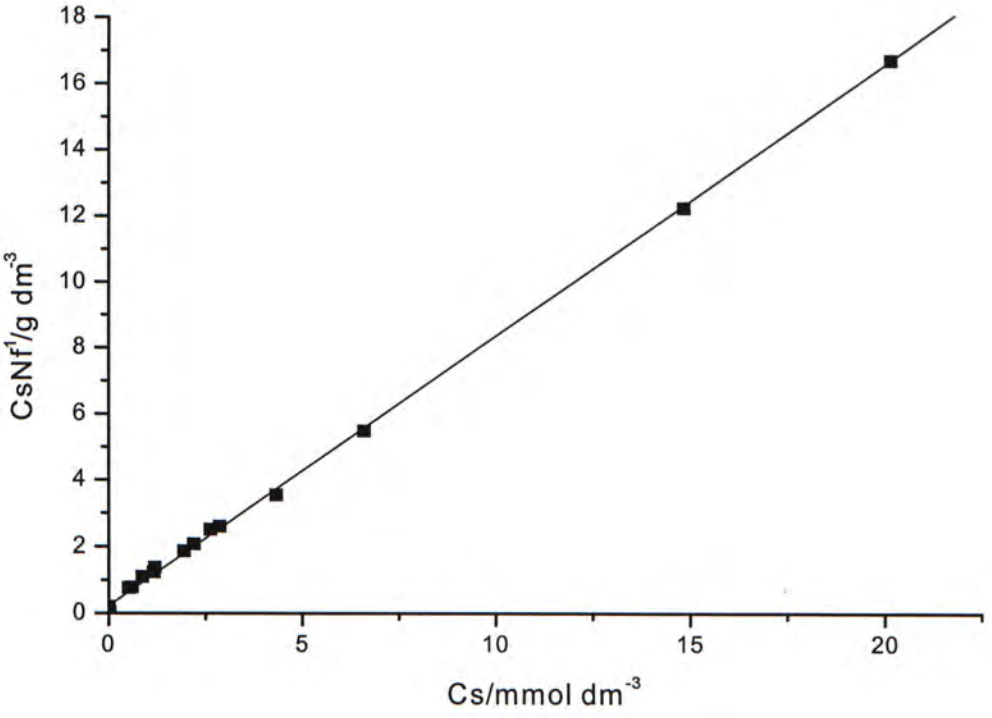


Figure 12. Linearization of the adsorption isotherm of the Mo(VI) on polysiloxane surface.

Among the various oxidation states, Mo(VI) is most stable. Mo(VI) species in aqueous media exist as the monomeric MoO_4^{2-} in basic solutions. However, various polymerizd species[121], such as $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$ and $Mo_8O_{26}^{4-}$ are successively formed with decreasing pH as the concentration of Mo(VI) is greater than 10^{-3}mol/L. When the concentration of Mo(VI) is as low as 1 ppb, decreasing the pH will produce $HMoO_4^-$ and H_2MoO_4 as the main species[122]. This species may adsorb on the polysiloxane by the interactions shown in Figure 13. The polymeric species will depolymerize before adsorption[123]. These interactions are similar to those between EDTA[124] and Mo(VI) or IDA[125] and Mo(VI) proposed by the other chemists. The high

adsorption capacity is mainly due to the high availability of the nitrogen and oxygen atoms on the polysiloxane for the co-ordination of Mo(VI), while the high selectivity of Mo(VI) is attributed mainly to the combination of both the immobilized ligand and the base matrix.

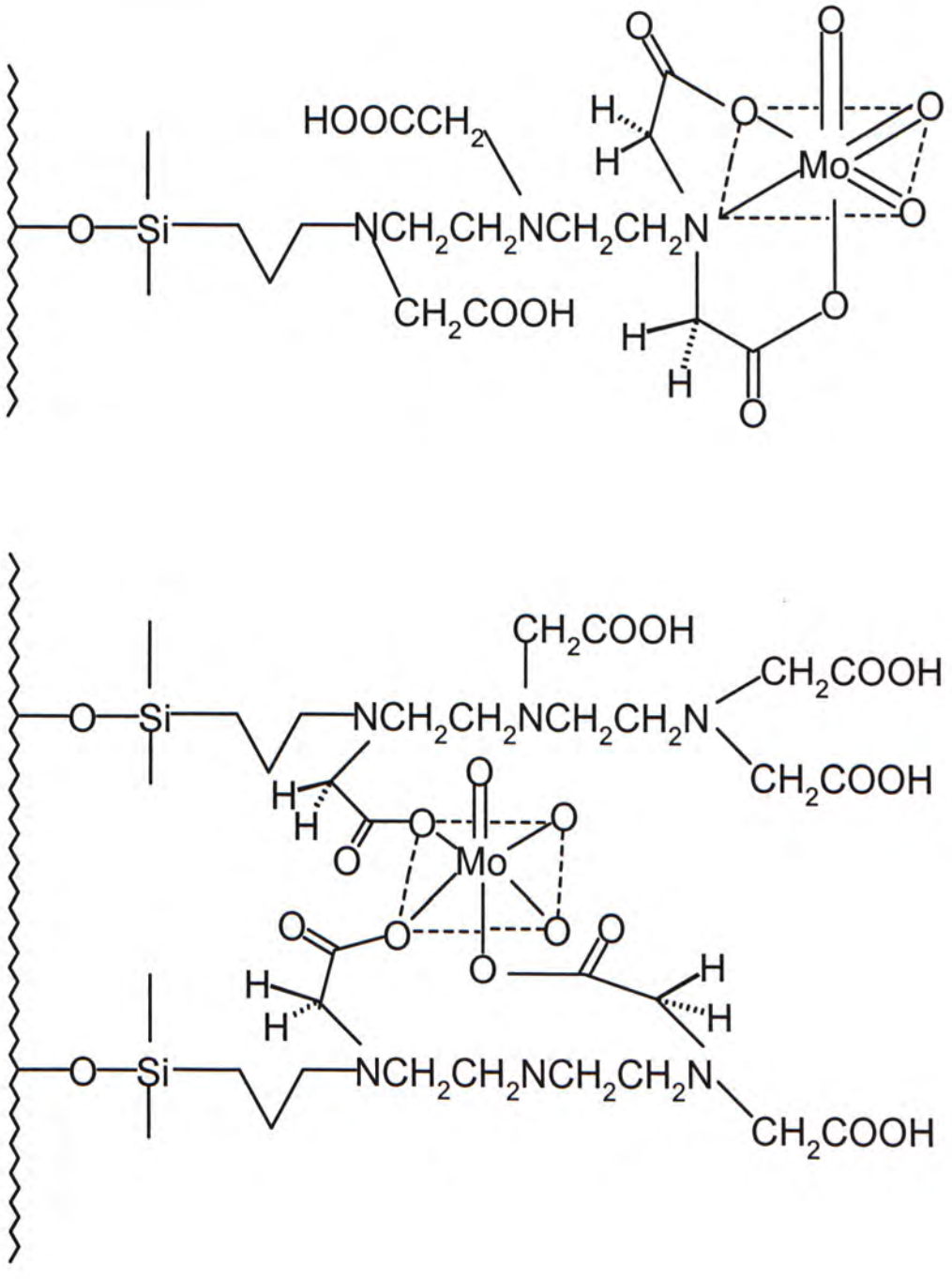


Figure 13. Proposed scheme for adsorption of Mo(VI) from water onto the polysiloxane surface.

3.7 Desorption Studies

To be useful for preconcentration, the Mo(VI) adsorbed by the polysiloxane should be easily released under mild conditions. Nitric acid has emerged as one of the most suitable materials for the recovery of Mo(VI) from the polysiloxane. The desorption of Mo(VI) from metal loaded polysiloxane was studied using different concentrations of nitric acid. The recovery of Mo(VI) as a function of nitric acid concentration is shown in Figure 14. It shows that Mo(VI) is desorbed quantitatively at acid concentrations higher than 2M. Hence, 2M nitric acid was selected for the desorption of Mo(VI).

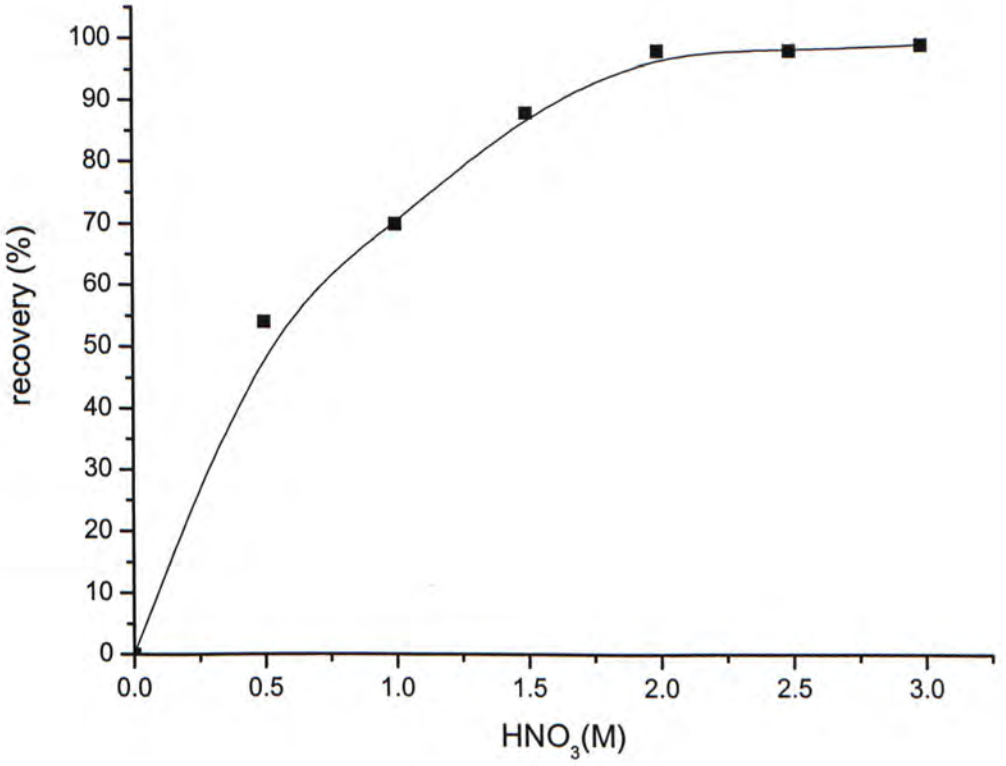


Figure 14. The concentration of nitric acid for desorption of Mo(VI).

3.8 Effect of Foreign Ions on Preconcentration

The effects of foreign ions usually found in seawater were examined using 250 mL of 10 ppb molybdenum solution and excess amount of matrix ions. The experimental results are given in Table 3. It shows that sodium(I), potassium(I), magnesium(II), calcium(II), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), iron(II), cadmium(II), tungsten(VI), aluminum(III), strontium(II), barium(II), chloride, fluoride, bromide, iodide, perchlorate, thiocyanate, silicate, sulphate, nitrate dihydrogenphosphate and hydrogenphosphate ions do not interfere with the determination of molybdenum solution by this preconcentration method. The most serious interferences are from chromium(III), iron(III), lead(II) and tin(VI). Interferences from these ions are probably due to their stronger complex formation than Mo(VI). However, the concentration of these metal ions in seawater are normally much lower than Mo(VI). Therefore, Mo(VI) in seawater can be recovered quantitatively using the proposed procedure. In order to eliminate the interferences of iron(III), ascorbic acid is used as a masking agent. Only 0.1g of it is required to reduce a 3000-fold excess of iron(III) to iron(II) before preconcentration, as indicated previously. A 98% recovery of Mo(VI) in excess concentration of iron(III) can be achieved after adding ascorbic acid[104].

Table 3: Effect of foreign ions

Ion	concentration	Added as	Recovery
Na(I)	1.3×10^5 ppm	NaCl	93%
K(I)	4.6×10^3 ppm	KCl	98%
Mg(II)	3.3×10^3 ppm	$MgCl_2$	93%
Ca(II)	4.6×10^3 ppm	$CaCl_2 \cdot 2H_2O$	101%
Mn(II)	30ppm	$MnSO_4 \cdot H_2O$	103%
Fe(II)	30ppm	$FeCl_2 \cdot 4H_2O$	96%
Co(II)	30ppm	$Co(NO_3)_2 \cdot 6H_2O$	105%
Ni(II)	30ppm	$NiCl_2 \cdot H_2O$	102%
Cr(III)	30ppm	$Cr_2(SO_4)_3 \cdot 15H_2O$	72%
Cu(II)	30ppm	$Cu(NO_3)_2 3H_2O$	94%
Zn(II)	30ppm	$ZnCl_2$	102%
Pb(II)	30ppm	$Pb(NO_3)_2$	75%
Fe(III)	30ppm	$FeCl_3 \cdot 6H_2O$	14%
Cd(II)	30ppm	$CdCl_2.H_2O$	98%
Sn(IV)	30ppm	$SnCl_4.5H_2O$	11%
W(VI)	30ppm	$Na_2WO_4 \cdot 2H_2O$	101%
Al(III)	30ppm	$Al(NO_3)_3 \cdot 9H_2O$	105%
Sr(II)	30ppm	$SrCl_2 \cdot 6H_2O$	105%
Ba(II)	30ppm	$BaCl_2 \cdot 2H_2O$	99%
Cl^-	1.3×10^5 ppm	NaCl	93%
F^-	30ppm	KF	95%
Br^-	30ppm	NaBr	105%
I^-	30ppm	NaI	102%
ClO_4^-	30ppm	$KClO_4$	99%
SCN^-	30ppm	KSCN	98%
SiO_3^{2-}	30ppm	$Na_2SiO_3 \cdot 9H_2O$	105%
SO_4^{2-}	30ppm	Na_2SO_4	101%
NO_3^-	30ppm	$Co(NO_3)_2 \cdot 6H_2O$	105%
$H_2PO_4^-$	30ppm	NaH_2PO_4	101%
HPO_4^{2-}	30ppm	$Na_2HPO_4 \cdot 12H_2O$	104%

3.9 Effect of Flow Rate on the Recovery of Mo(VI)

In order to define the efficiency of adsorption of Mo(VI) on the polysiloxane column, Mo(VI) (50mL, 10ppb) solutions at pH 3 were passed through the column at various flow rates from 0.2 to 2mL/min, and the recoveries were determined by using 2M nitric acid as an eluent. The results are given in table 4. It was found that the recovery was > 95% when the maximum flow rate of 2mL/min was used, indicating rapid and quantitative adsorption of Mo(VI) on the polysiloxane column. Faster flow rates could not be investigated due to high back-pressure generated by the columns and further engineering modification is required to withstand a higher pressure operation.

Table 4: Effect of flow rate on the recovery of Mo(VI)

Flow rate (mL/min)	0.8	1.2	1.3	1.7	2
Recovery (%)	97 ± 2	94 ± 3	97 ± 2	99 ± 2	97 ± 1

3.10 Reusability of the Column

The polysiloxane column was subjected to sixteen cycles of loading and elution. An initial amount of Mo(VI) (50 mL, 10 ppb) was employed to load the resin. In each cycle, the adsorption was carried out at pH 3 and at a flow rate of 2 mL/min, while the desorption was performed by using 5 mL of 2M HNO_3. The polysiloxane was able to withstand the acidic conditions, and its metal-ion-binding ability was retained after repeated 2M HNO_3 treatment. Figure 15 shows the results of these studies confirming that the column could be reused economically and environmentally for the preconcentration of Mo(VI).

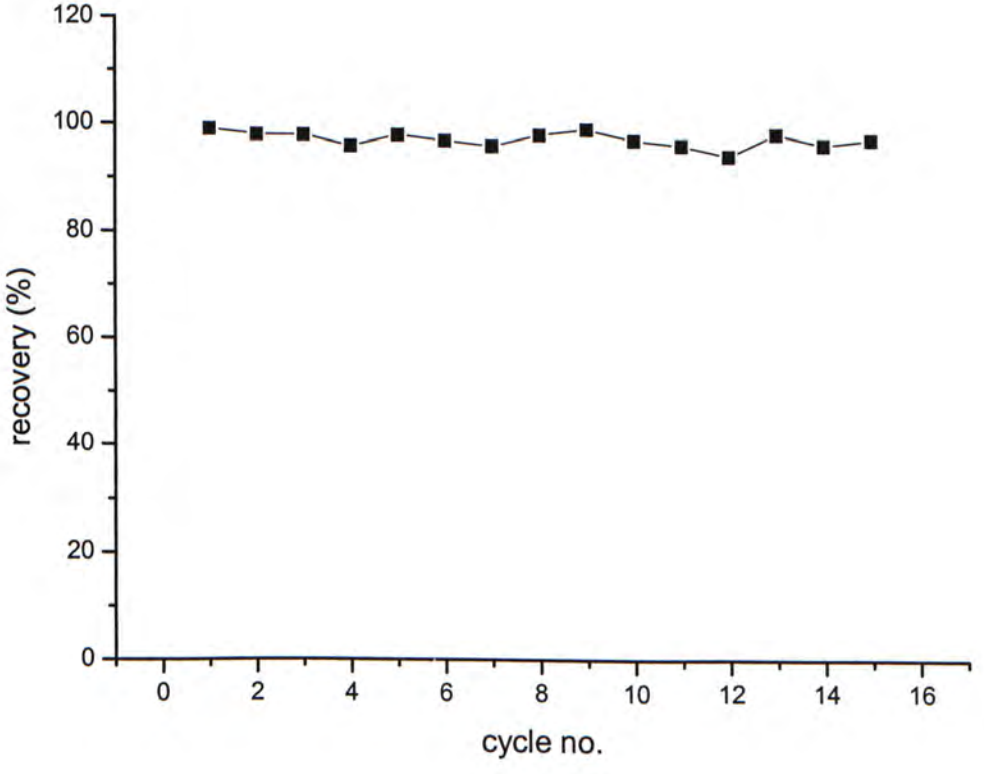


Figure 15. Evaluation of the reusability of mini-column on preconcentration of Mo(VI)

3.11 Preconcentration Factor

The preconcentration factor was determined by passing 500 mL of 10 ppb Mo(VI) through the polysiloxane column, and the smallest amount of 2M HNO_3 used for achieving 95% or above recovery of Mo(VI) was determined. Since as little as 5 mL of eluent is enough for the removal of Mo(VI), the preconcentration factor is 100. As we mentioned that the sensitivity of the ICP-AES is not sufficiently high enough for the detection of trace amount of Mo(VI) in seawater, this preconcentration factor makes direct determination possible.

3.12 Detection Limit

The detection limit (DL), the lowest concentration level that can be determined to be statistically different from a blank, are calculated from three times the standard deviation (σ) of the blank water at pH 3.

DL (ppb) = 3 x σ

In this study, five replicate measurements of the blank water at pH 3 were evaluated. The detection limits for Mo(VI) was found to be 0.17 ppb.

3.13 Accuracy

The accuracy of this proposed method was evaluated by determining the concentration of Mo species in certified standard reference materials (National Research Council of Canada CASS-2 and NASS-2), and comparing the certified values with the measured values. Results are shown in Table 5. A good agreement between the measured values and the certified values was obtained using the proposed method. From these results, it can be concluded that the method developed for preconcentration and determination of Mo(VI) is accurate, reliable and reproducible. The accuracy of the proposed method for preconcentration of Mo(VI) was also demonstrated by determining the recoveries of Mo species spiked into seawater samples, which will be discussed in the following sections.

Table 5: Analytical results of molybdenum determination in CRMs (n=5)

Sample	CASS-2	NASS-2
Found (ppb)	8.27 ± 0.22	8.71 ± 0.22
Certified value (ppb)	8.78 ± 0.86	9.6 ± 1

The uncertainty is based on a 95 percent confidence limit for the mean.

3.14 Determination of Mo(VI) in Seawater Samples

Water samples were collected from the Tolo Harbour in Hong Kong and analyzed according to the recommended procedure (column method) for preconcentration and ICP-AES determination. The verification of the proposed system for preconcentration of Mo species was further demonstrated by determining the recovery of Mo(VI) spikes added into the seawater samples. The results are given in Table 6. The measured concentrations of Mo spikes in seawater samples were in good agreement with the amounts added, indicating that the applicability of the proposed method for seawater analysis.

Table 6: Determination and recovery of molybdenum in seawater (n=5)

Sample[a]	Mo(VI) added (μg)[b]	Achieved Molybdenum (ppb)	Recovery (%)	RSD (%)[c]
Tolo Harbour	0	7.19		3
	0.5	8.82	96	

[a]Sample volume: 250mL.

[b]Mass of added molybdenum in 250mL of sample volume.

[c]Relative standard deviation.

3.15 Precision

The precision of the proposed method was expressed as relative standard deviation (RSD). The precision of the method was obtained by five replicate analyses of seawater samples. Relative standard deviations for Mo(VI) was 3.06%.

CHAPTER 4 CONCLUSION

A new method for preconcentration and separation of trace amounts of molybdenum in seawater samples prior to the determination by inductively coupled plasma atomic spectroscopy was reported. Diethylenetriaminetetraacetic acid functionalized polysilxoxane was successfully synthesized and characterized by NMR spectrometer, FT-IR spectrometer and elemental analysis.

The preconcentration of Mo(VI) using the polysiloxane was systematically investigated. The pH values of molybdenum solution played an important role in the adsorption process. Maximum adsorption was obtained at pH 3, whereas molybdenum can also retain on polysiloxane in the weakly acidic or neutral region with lower adsorption. The total adsorption capacity of the polysiloxane, which was determined by a batch process at pH 3, was found to be 1.2mmolg^{-1}. Since a small loading of the polysiloxane mini-column can be reused over ten times without losing its preconcentration ability, application of the diethylenetriaminetetraacetic acid functionalized polysiloxane for preconcentration of Mo(VI) is economical and efficient. The equilibrium time, which was investigated by batch experiments at pH 3, was found to be less than 5 minutes. The fast extraction rate indicates that there is a high availability of the chelating groups, and most of them are present on or near the surface of polysiloxane and thus allows rapid kinetics. Possible interactions between polysiloxane and Mo(VI) were proposed. Nitrogen and oxygen atoms were considered to be the main functional group atoms for chelate formation. By studying the adsorption isotherm of molybdenum, we conclude that the adsorption process

conforms to the Langmuir model. In order to preconcentrate Mo(VI) in seawater samples, we have to ensure that the seawater salts do not interfere with the adsorption of polysiloxane. We found that most ions except Cr(III), Fe(III), Pb(II) and Sn(VI) did not interfere with the determination of molybdenum solution by this preconcentration method. However, it should be noted that the concentrations of these interfering metal ions in seawater are normally much lower than that of Mo(VI).

The precision of the preconcentration method, calculated as the relative standard deviation of seawater samples was 3%. The preconcentration factor and detection limit were 100 and 0.17 ppb respectively. The accuracy of the proposed method was evaluated by determining the concentration of Mo species in certified standard reference materials. Measurement results were in good agreement with the certified values, indicating that this method for preconcentration and determination of Mo(VI) is accurate and reliable.

The diethylenetriaminetetraacetic acid functionalized polysiloxane is efficient to separate and preconcentrate molybdenum from seawater when it is used as a packing material in the mini-column. In comparison with other procedures proposed in the literature, this column method has the advantages of simplicity, rapidity and a high preconcentration factor. In addition, the polysiloxane is stable in acidic solution and having high reusability. For real water samples having a relatively high concentration of iron(III), a reducing agent such as ascorbic acid should be added prior to the preconcentration. This new method can be coupled to ICP-AES using a flow-injection analysis (FIA) system for on-line preconcentration analysis.

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